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13. ABSTRACT (Maximum 200 words)

An experimental set up has been designed and built for the acquisition of ultrafast second harmonic generation (SHG) measurements to monitor surface dynamics at electrified interfaces with special emphasis on processes induced by variations in the applied potential across single crystal metal-electrolyte solution interfaces. Much of the effort has been devoted to the study of reactions of interest to fuel cells, including hydrogen and CO adsorption, as well as methanol oxidation on Pt surfaces. As evidenced by the experimental results obtained, the feasibility of measuring transient effects is limited by the geometry of the cell and particularly by the electrode size. Attempts to overcome these problems are being made by using single crystal ultramicroelectrodes taking advantage of spontaneous facetting to allow single crystalline microsurfaces to be examined optically without interference from other areas of the electrode.

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IN SITU AND EX SITU NON LINEAR OPTICAL TECHNIQUES AS APPLIED TO THE STUDY OF ELECTRODE MATERIALS FOR ENERGY STORAGE ENERGY GENERATION AND ELECTROCATALYSIS

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A. INTRODUCTION

The rather recent development of pulsed lasers in the UV-visible region has opened new prospects for acquiring time-resolved information regarding chemical kinetics and reactivity with unparalleled level of detail. Much of the equipment purchased under this research contract has been incorporated into a complex instrumental array aimed at monitoring dynamic events at electrified interfaces using primarily second harmonic generation (SHG)[1]. This specific technique is sensitive to the electronic properties of the interface, which, in turn, are a function of the state of charge of the surface, the second order polarizability tensor of adsorbed molecules, and interactions thereof. Much of the effort, so far, has been devoted to the study of reactions of interest to fuel cells including hydrogen and CO adsorption, as well as methanol oxidation on Pt surfaces. The following sections summarize the results of experiments performed during this reporting period using single crystal Pt(100) surfaces aimed at assessing the performance of the overall instrumental array.

B. EXPERIMENTAL ASPECTS

Optics. Light pulses were generated from a dye laser (Coherent model 702-2) coupled to a cavity dumper (Coherent model 7220) pumped by a frequency-doubled mode-locked Nd:YLF laser (Coherent model Antares 76-YLF). A schematic diagram of the entire optical system is shown in Fig. 1. The temporal behavior of the system was measured with an autocorrelator (Coherent model FR 103) and monitored on a digital oscilloscope yielding 3 ps (HWFH) pulses with a repetition rate of 8 MHz. The dye laser wavelength was set 592 nm, as determined by a monochromator (Jobin-Yvon H-10). The output power was measured with a power meter (Coherent Fieldmaster) yielding typical values of about 80 mW. The overall response of the laser system was found to be stable for prolonged periods of time; hence, no reference line was used to normalize against power fluctuations.

As shown in Fig. 2, the laser beam was directed upward by 30° using a regular aluminum mirror impinging normal to one of the electrochemical cell side silica windows and 60° with respect to the normal to a single crystal Pt(100) attached to a specially designed holder. Prior to reaching the electrode surface, the beam was tightly focused using a 85 mm lens mounted on an XYZ translator, while monitoring the SHG output

until maximum response was achieved. The beam emerging through the cell window was passed through a polarizer, to control the output polarization, a UV filter (Schott UG11) to remove the fundamental frequency, and then focused by a 100 mm fused silica lens on the entrance slit of a monochromator (Jobin-Yvon H-10) set at a wavelength of 291 nm, i.e. half that of the fundamental original frequency. Based on careful measurements, the output light was found to contain a very sharp maximum at precisely that wavelength with no evidence for other spurious signals. The monochromator output was attached to a photomultiplier tube (Hamamatsu R 928) supplied with a nominal voltage of 1250 V. The signal from the photomultiplier was fed to a Gated Photon Counter (Stanford Research Systems SR 400) with the discriminator voltage level set at –10 mV, which was in turn fed through a fast amplifier to a PC equipped with pulse counting software (EG&G Ortec ACE-MCS Multichannel scaler, version 1.4) allowing pulses to be accumulated in 4096 separate time windows (gates) with no dead time between windows. The window range was controlled via software with minimum value (dwell time) of 2 μs. The software allowed for multiple scans to be added together and stored as one data set. Unfortunately, the photon counter was found to be too slow for μs time resolution experiments, and was only used while adjusting the optics.

The SHG signal showed as expected a quadratic dependence on the incoming light intensity before reaching saturation level for high values. No surface damage due to laser light was discerned after the SHG measurements. All experiments were performed with p-input and p-output polarizations.

Spectroelectrochemistry. An all-Teflon electrochemical cell shaped in the form of an extruded hexagon was used for all the experiments described in this report. As shown in Fig. 2, four cylindrical orifices were machined at 60° with respect to one another on adjacent flat ends of the hexagon. These of these were covered with flat quartz windows, allowing the laser beam to impinge on the surface at a 60° angle with respect to the surface normal and also visual access to the electrode from the bottom. The fourth orifice was used to house a single crystal electrode mounted vertically using a collet to enable a hanging meniscus to be formed. This arrangement minimizes contributions due to the electrochemical response induced by the walls of the crystal. The internal volume of the cell was of about 25 cm^3. The counter electrode was a platinum foil located close to the bottom window (not shown in the figure) a distance of approximately 1.5 cm. The reference electrode (SCE) was connected to the main cell compartment through a Luggin capillary. A thin Teflon tube delivered either inert gas (Ar) or CO to the electrolyte solution. Potentials were controlled with a EG&G PARC model 175 programmer and a model 173 potentiostat using a separate signal generator to allow synchronous SHG and electrochemical data acquisition.

The slightly facetted single crystal surface Pt (100) was prepared by annealing in a hydrogen/ oxygen flame, followed by cooling in a stream of ultrapure argon and then covered with a drop of ultrapure water to avoid contact with the atmosphere during transfer. Once in the cell, the crystal surface was oriented to achieve maximum signal output. Although not as yet attempted this configuration should be suitable for

performing rotational anisotropy measurements. All chemicals including the water and gases were of ultrahigh high purity.

C. RESULTS AND DISCUSSION

Figure 3 shows plots of the second harmonic generation (SHG) signal obtained for a slightly facetted Pt(100) electrode in 0.1 M $HClO_4$ solution (lower panel) while scanning the potential linearly in the range –0.2 to 1.2 V vs SCE. The electrochemical response, given in the upper panel in this figure, is, by and large, characteristic of Pt (100) in this electrolyte solution, as judged by a comparison with data published elsewhere[2]. As reported by other authors, the magnitude of the SHG signal was found to increase significantly at about 0.0 V, which coincides with the onset of adsorption of strongly bound hydrogen on the surface[3].

In addition to the high contrast in the SHG response induced in the presence and absence of adsorbed atomic hydrogen on the Pt surface the adsorption/desorption kinetics are extremely fast. These characteristics provide ideal conditions to monitor optically the time constant of the cell. For these experiments, a potential step was applied to the Pt(100) electrode polarized at +0.50 V, a potential at which the SHG response is minimal to -0.20 V, a potential at which the coverage of strongly adsorbed hydrogen is significant and thus the SHG signal is very large. As indicated in Fig. 4, a plot of the SHG signal vs time following application of the potential step (see arrow) was characterized by an initial linear increase followed by a smooth transition region to the steady state SHG value at – 0.20 V. It is obvious from the transient behavior observed that the overall electrical response of the system is <u>not</u> controlled by the surface kinetics, but rather by the electrochemical cell itself for which the RC constant is on the order of 10 ms.

Equally large increases in the SHG signal were observed upon adsorption of CO on Pt(100) in the same electrolyte saturated with CO. This is particularly evident in Fig. 5, which compares the cyclic voltammetry (upper panel) and SHG signals (lower panel) recorded simultaneously. As clearly indicated, the oxidation of adsorbed CO at ca. 0.6 V vs SCE, is accompanied by a sudden decrease in the SHG signal from ca. 2000 to 500 counts. As a final illustration of the capabilities of the system, Fig. 6 shows SHG signals obtained while cycling a Pt(100) electrode in a 25 mL 0.1 M $HClO_4$ solution containing 50 μL CH_3OH, where the SHG response tracks the surface coverage of CO generated via the interaction of methanol with the surface as originally reported by Bae[4].

D. FUTURE PROSPECTS

As illustrated by the results shown in the previous section, access to faster time domains for the study of interfacial processes is inextricably linked to the design of cells with very short time constants. Since the capacitance is directly proportional to the size of the electrode it becomes imperative to use ultramicroelectrodes to accomplish the desired goals[5]. Although the preparation and characterization of electrodes of sub-micron dimensions may be regarded as routine, the control of the surface micro-topography continues to pose a formidable challenge. The approach being explored at

CWRU involves the use of single crystal microspheres prepared by the same method described by Clavilier et al. for much larger single crystal specimens[6]. As described by these authors, controlled cooling of a melted sphere at the end of a wire induces crystallization and the development of clearly defined low index facets often arranged on the surface in very specific geometric patterns. Excellent results have been obtained so far in this laboratory with this method for preparing facetted microspheres, ca. 0.1 mm in diameter devoid of imperfections due to polishing. It becomes then possible to illuminate the sphere with a collimated laser beam and identify sharp reflections from individual facets. The electrochemical response of a microsphere electrode fully immersed in an electrolyte will invariably contain contributions derived from its entire surface. However, the optical response associated with perfect single crystal facets can be clearly identified by illuminating the sphere with collimated laser and searching for strong reflected spots.

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F. FIGURE CAPTIONS

Fig. 1. Schematic diagram of the optical system for *in situ* SHG measurements constructed in our laboratory.

Fig. 2. Schematic diagram of the spectroelectrochemical cell for rotational anisotropy second harmonic generation measurements of single crystal electrodes in the hanging meniscus configuration at an angle of incidence of 60^{o}.

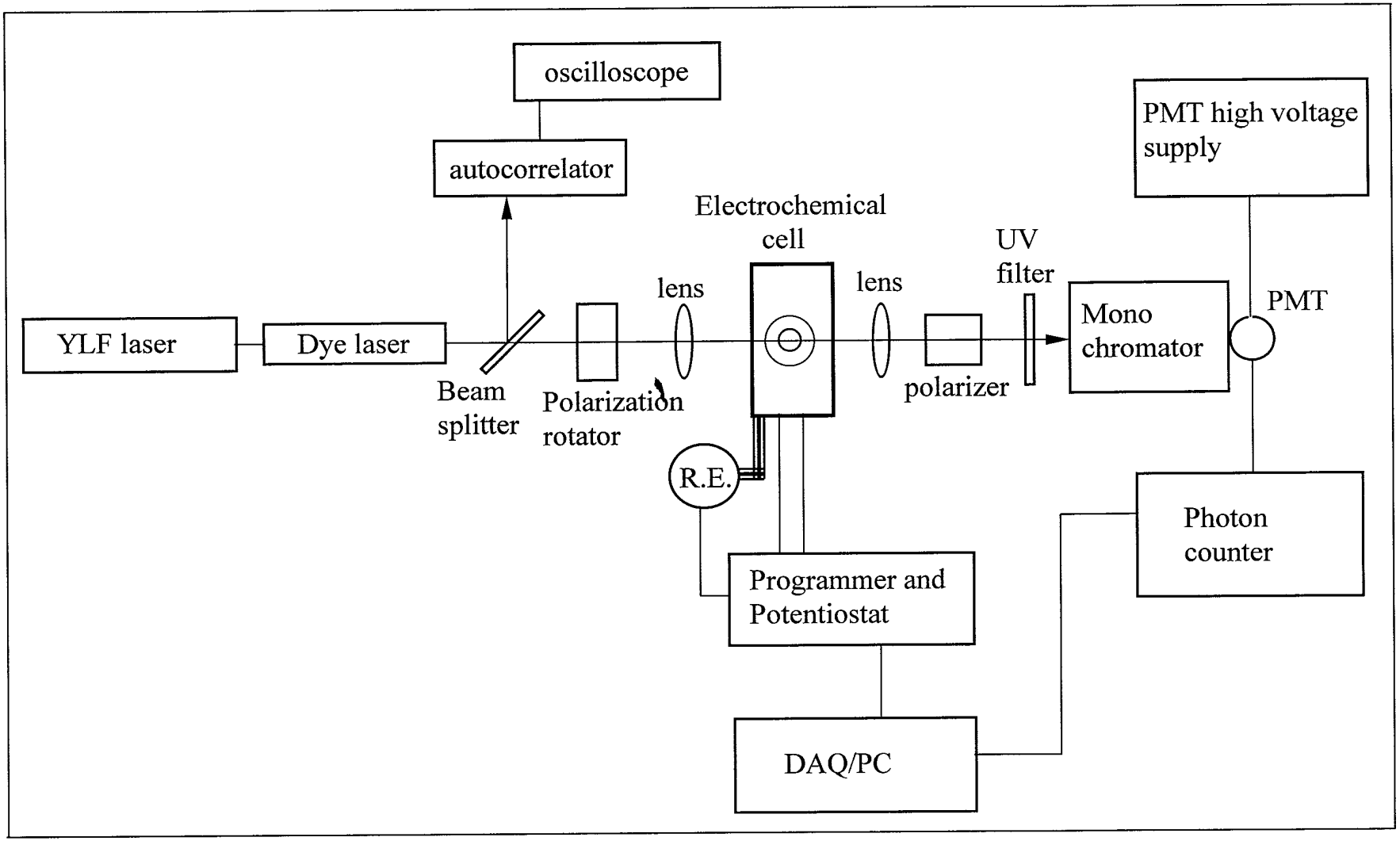
Fig. 3. Cyclic voltammetry (upper panel) and second harmonic generation signal (lower panel) obtained simultaneously for a Pt(100) electrode in 0.1 M $HClO_4$ solution in the range –0.2 to 1.2 V vs SCE. Scan rate: 50 mV/s. Electrode area: 0.32 cm^2.

Fig. 4. Transient SHG response following application of a potential step from +0.50 to –0.20 V at the time indicated by the arrow to a Pt(100) electrode. Other conditions are specified in caption, Fig. 3.

Fig. 5. Cyclic voltammetry (upper panel) and second harmonic generation signal (lower panel) obtained simultaneously for a Pt(100) electrode in a CO saturated 0.1 M $HClO_4$ solution in the range –0.2 to 1.2 V vs SCE. Scan rate: 50 mV/s. Electrode area: 0.32 cm^2.

Fig. 6. Cyclic voltammetry (upper panel) and second harmonic generation signal (lower panel) obtained simultaneously for a Pt(100) electrode in an Ar-purged 0.1 M $HClO_4$

solution with 50 μL methanol added, in the range –0.2 to 0.8 V vs SCE. Scan rate: 20 mV/s. Electrode area: 0.32 cm^2.



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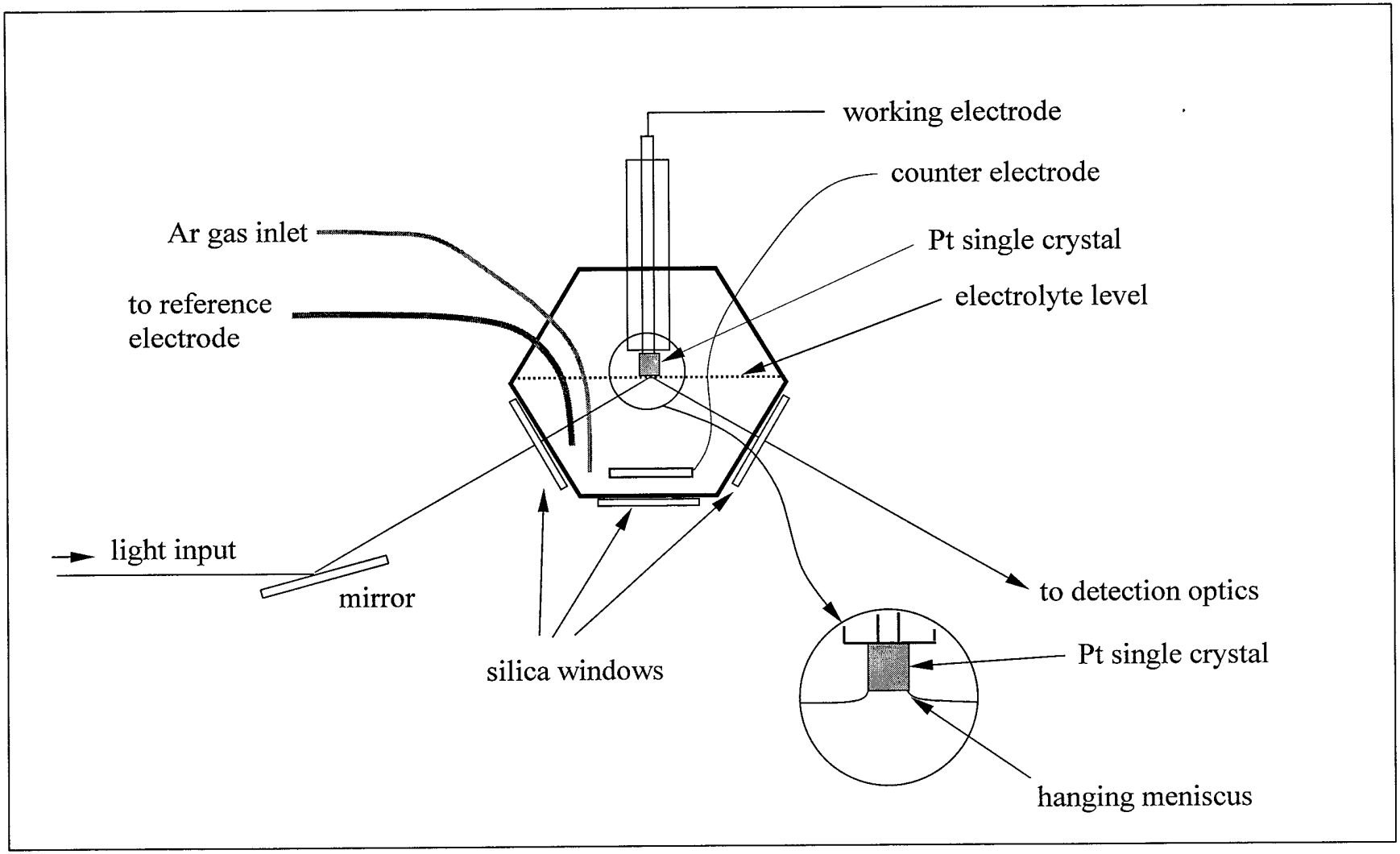

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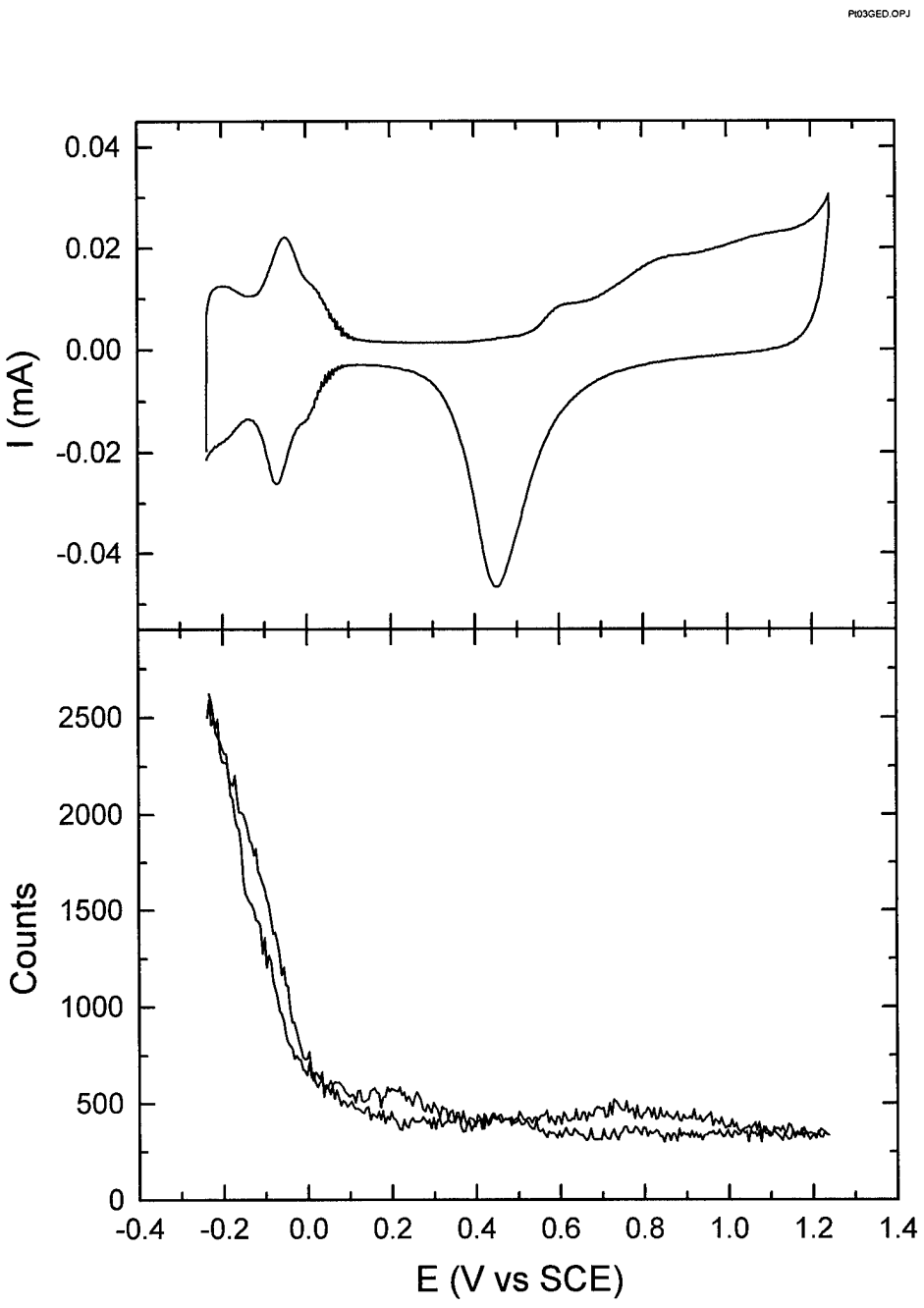

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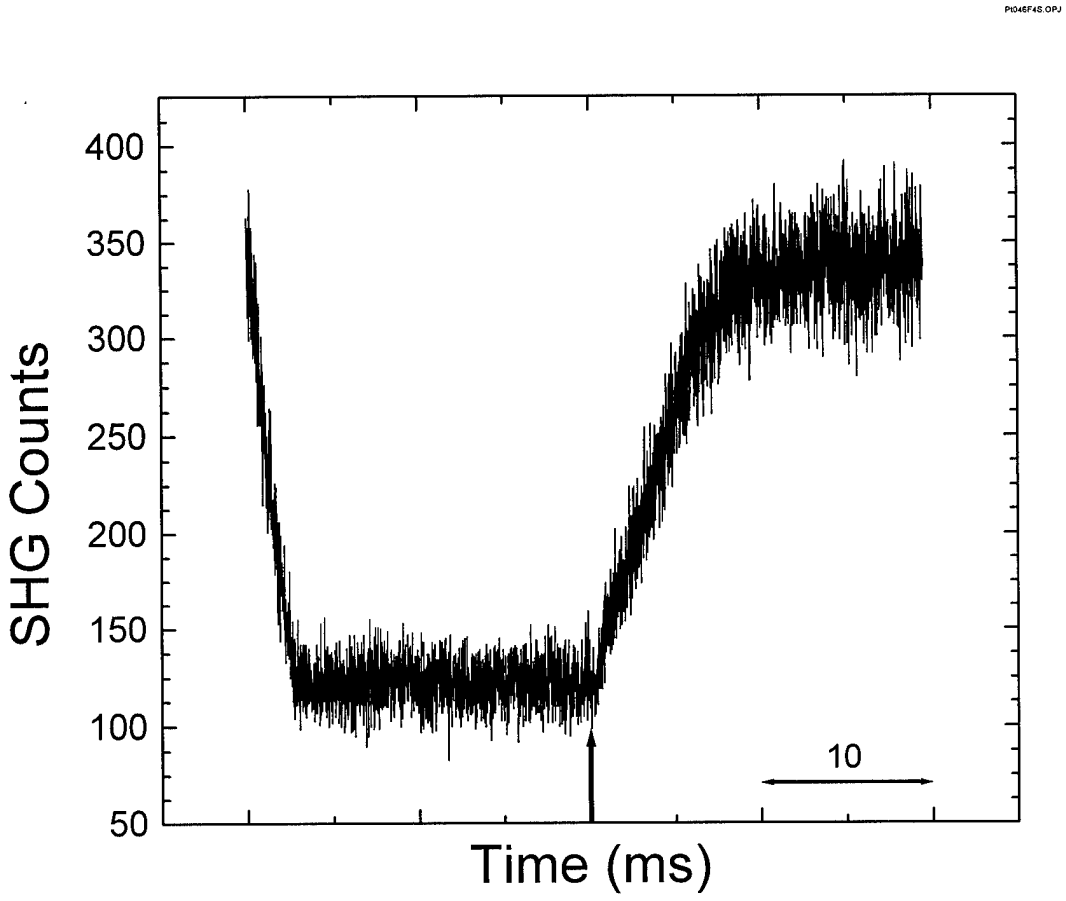

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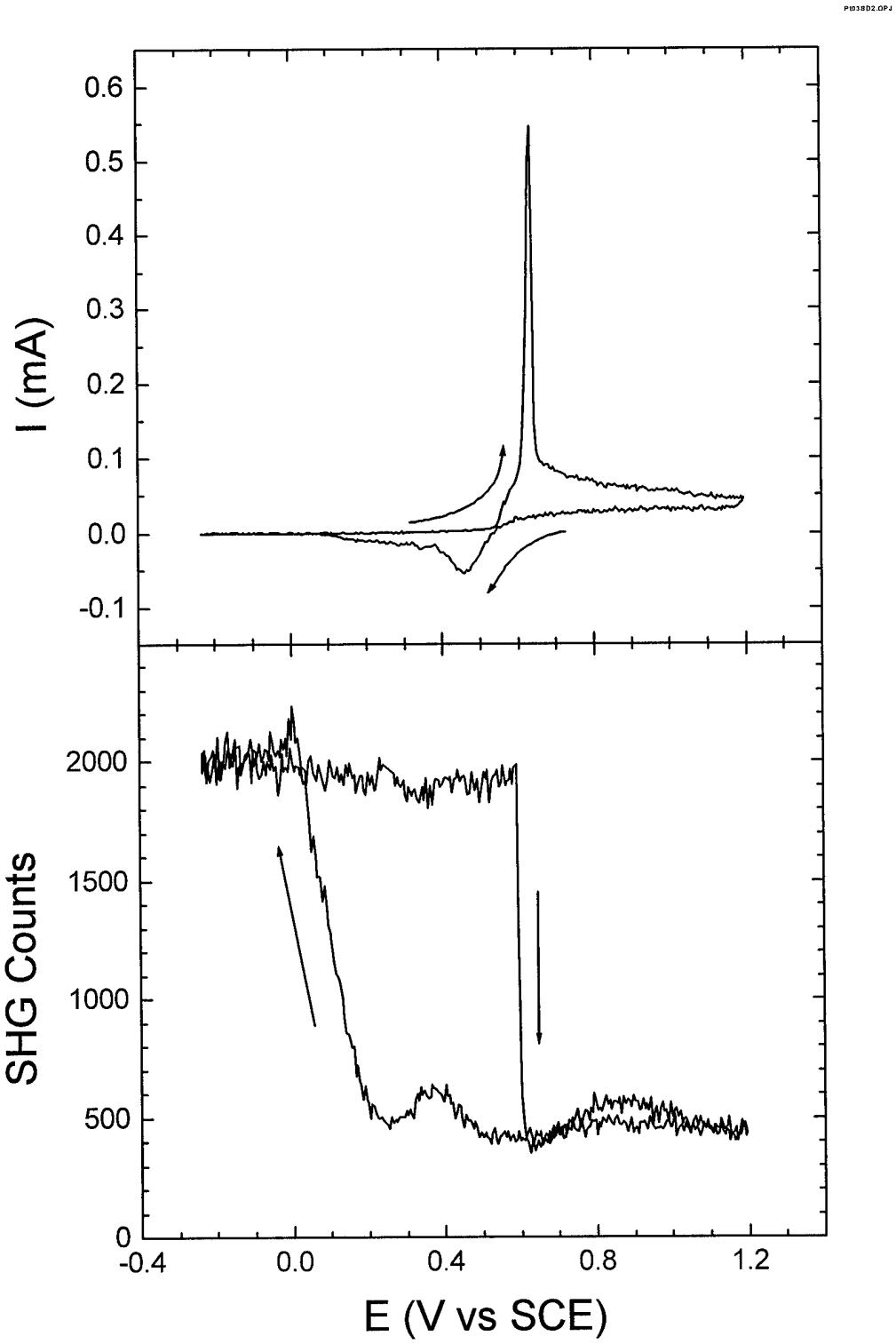

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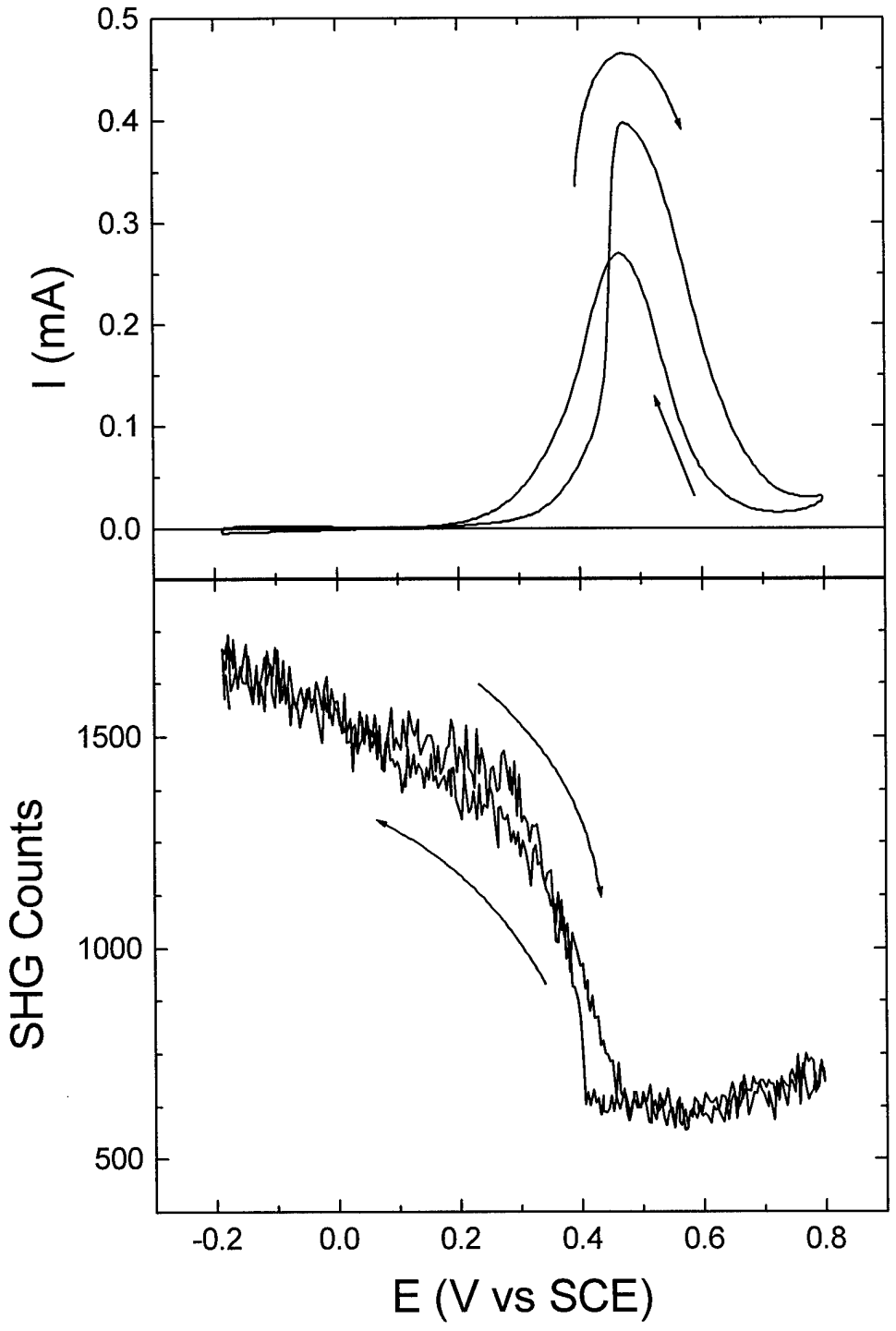

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